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Anti-Stokes-enhanced tunneling ionization of molecules

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We consider the influence of vibrational motion of nuclei on the tunneling ionization of a molecule in a strong light field. Unlike the molecular Ammosov-Delone-Krainov (MO-ADK) model [X. M. Tong *et al.*, Phys. Rev. A **66**, 033402 (2002)], the Franck-Condon factors that take into consideration the quantization of nuclear vibrations are introduced in the theory. Modification of the vibrational motion of nuclei by the external field leads to the time-dependent constant in the asymptotic form of the electronic wave function. This in turn leads to a more significant modification of the Keldysh theory for the tunnel effect in molecules as compared to the MO-ADK model. We take into account the possibility of vibrational quantum numbers changing in a neutral molecule and in a molecular ion in the process of the tunneling ionization, which in principle enables one to get molecular ions of a certain isotopic composition if the vibrational states of the neutral molecules with this isotopic composition are pumped before ionization. We present numerical results illustrating this possibility for the isotopes of a hydrogen molecule.

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I. INTRODUCTION

The ionization of molecules by a laser field has been investigated extensively both theoretically and experimentally. For a sufficiently intensive laser field of a frequency that is not very high (appropriate estimates are given below) this ionization occurs in the tunneling regime. The availability of vibrational and rotational degrees of freedom of molecules leads to a larger number of possible effects accompanying the tunneling ionization of molecules compared to the tunneling ionization of atoms. One of these effects connected with the vibrational degrees of freedom is examined in this paper.

In the tunneling removal of an electron from a molecule, the molecular ion can occur in the ground vibrational as well as in excited vibrational states. In terms of energy, it is clear that the ion formation probability in one of the excited vibrational states is less than the probability of its formation in the ground vibrational state. The appropriate calculations were performed in Ref. [1]. By analogy with the Raman effect, such a decrease of the tunneling rate can be called Stokes attenuated. However, if initially a neutral molecule is in an excited vibrational state, then after the tunneling removal of an electron a molecular ion can occur in the ground vibrational state. Again, as regards energy, it is clear that the tunneling rate will be greater than the tunnel effect rate for a neutral molecule in the ground vibrational state. Such an increase of the tunnel effect rate can be called anti-Stokes enhanced.

The reasons for the occurrence of a molecule in the excited vibrational state at the moment of tunneling ionization may be different, for example, for a high temperature of molecular gas or a thermodynamically unbalanced population of molecular vibrational levels formed as a result of a chemical reaction. Purposively prepumping the excited vibrational states due illumination by resonance IR radiation is also possible. In the latter case the anti-Stokes-enhanced tunneling ionization may be useful for the laser isotope separation [2–4]. In this paper this possibility is demonstrated by an example of hydrogen isotopes.

Note that the analogous phenomenon in ordinary single-photon molecular ionization was described in Ref. [5]. The vibrational excitation of a molecule shifts the photoelectric threshold to the long-wave region.

Several remarks should be made now concerning the accuracy of the method of taking into account the core excitation or deexcitation in the tunnel effect proposed in Ref. [1]. The development of this method made it possible to include many-body effects into the theory of the tunnel effect in atoms [6–9]. In turn, the many-body effects made it possible to explain the large number of experimental results [10–12]. In a recent paper [13] good agreement between the method proposed in Ref. [1] and the time-dependent Schrödinger equation numerical solution [14] was demonstrated.

In this paper we restrict consideration to a hydrogen molecule to make it possible to use the most illustrative analytical methods. In Sec. II the electronic wave functions are constructed in the neutral hydrogen molecule and its positive ion by the variational method. In Sec. III the vibrational motion of molecules is considered in the Morse potential, the Dyson orbital is calculated, and the influence of a strong laser field on the vibrational molecular motion is taken into account, namely, on the magnitude of Franck-Condon factors. In Sec. IV the formula of the tunneling ionization rate is derived on the basis of the molecular Ammosov-Delone-Krainov (MO-ADK) model but with a more accurate account of vibrational motion. In Sec. V formulas are given for the ionization signal in the laser beam focus. In Sec. VI the results of calculation of the ionization signal are given for molecules with various isotopic composition in various initial vibrational states.

The atomic units are used hereafter, except in specified cases.

II. ELECTRON MOTION

The success of the Keldysh theory in describing the atomic ionization rate in a strong laser field (see, e.g., the review in Ref. [15]) stimulated the appearance of theoretical works

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devoted to the generalization of the theory on molecules. As is well known, the tunneling regime of ionization arises in the limit of the small Keldysh parameter γ,

$$\gamma^2 = \left(\frac{\kappa\omega}{F}\right)^2 \ll 1,$$

where ω is the carrier frequency of laser radiation, F is the amplitude value of the laser wave electric field, and $\kappa^2/2$ is the atomic ionization potential. This limiting case is also referred to as the ADK model [16].

In Ref. [17] the Keldysh theory was generalized to the case of the tunnel effect in Rydberg molecules including the polar ones, when the angular part of the wave function of the Rydberg electron is not a simple spherical function. In Ref. [18] the ADK model was used to describe the tunneling ionization of molecules in which the effective charge of the residual ion depended on the angle between the axis of the molecule and the direction of the light wave electric field. Thereby the anisotropy of the molecular core potential was taken into account. The most complete generalization of the tunneling ionization theory for molecules was carried out in Ref. [19] (the MO-ADK model); thus we will adhere to this work further in this section.

The MO-ADK model [19] requires using the valence electron wave function in the asymptotic form. For the ground state of the neutral hydrogen molecule and its positive ion the wave function in the single-electron approximation can be written in the form of an expansion in terms of the spherical functions Y_{lm},

$$\Psi(\mathbf{r}) = \mathcal{R}(r) \sum_{l=0,2,\ldots} C_l Y_{l0}(\hat{\mathbf{r}}), \quad \hat{\mathbf{r}} = \mathbf{r}/r,$$
$$\sum_l |C_l|^2 = 1, \tag{1}$$

where $\mathcal{R}(r)$ is the radial wave function corresponding to the electron binding energy $\kappa^2/2$. Its asymptotic behavior is determined by the expression

$$\mathcal{R}(r) \to C\kappa^{3/2}(\kappa r)^{1/\kappa - 1}e^{-\kappa r}, \quad r \to \infty. \tag{2}$$

We shall put forth the procedure of calculating the C_l coefficients, the κ parameter, and the C coefficient. Note that the influence of relativistic effects on the C constant was investigated in our recent research [20]. We shall use the direct variational method given in Ref. [21] as the basis of the calculation. We shall provide quantities relating to the hydrogen molecular ion with the index f and the neutral molecule of hydrogen with the index i.

A. Hydrogen-molecule ion

The Hamiltonian of a singly charged ion of the hydrogen molecule has the form

$$\hat{H}_f = -\frac{1}{2}\nabla_r^2 - \frac{1}{2M_a}\nabla_{R_a}^2 - \frac{1}{2M_b}\nabla_{R_b}^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R}.$$

Here $\mathbf{R}_i$ and M_i $(i = a,b)$ are the coordinate and the mass of the ith nucleus and $\mathbf{r}_i = \mathbf{r} - \mathbf{R}_i$ and $\mathbf{R} = \mathbf{R}_a - \mathbf{R}_b$ are vectors that are equal to the absolute value of the internuclear separation and specify the molecule orientation in space. For symmetric nonpolar molecules $\mathbf{R}_a = -\mathbf{R}_b$ and $R_a = R_b = R/2$.

In the Born-Oppenheimer approximation the electron wave function satisfies the stationary Schrödinger equation at a fixed R value,

$$\hat{H}_f^{(\mathrm{BO})}(R)\Phi_f(\mathbf{r};R) = E_f(R)\Phi_f(\mathbf{r};R), \tag{3}$$

where

$$\hat{H}_f^{(\mathrm{BO})}(R) = -\frac{1}{2}\nabla_r^2 - \frac{1}{r_a} - \frac{1}{r_b}.$$

In the simplest case of the variational method, the solution to Eq. (3) is chosen in the form of a superposition of two wave functions of the hydrogen-atom ground state with the centers in the corresponding nuclei,

$$\Phi_f(R,\mathbf{r}) = \frac{\gamma_f^{3/2}}{[2\pi(1+S_f)]^{1/2}}\left(e^{-\gamma_f r_a} + e^{-\gamma_f r_b}\right). \tag{4}$$

Here γ_f is the variational parameter that should be defined and S_f is the electronic overlap integral of the functions, centered on the different nuclei, giving the function (4) as normalized. This integral is obtained in prolate spheroidal coordinates [21]

$$S_f = S(\rho_f) = \left(1 + \rho_f + \tfrac{1}{3}\rho_f^2\right)e^{-\rho_f}, \quad \rho_f = \gamma_f R. \tag{5}$$

The γ_f parameter is found from the functional minimum condition

$$J_f(\gamma_f,R) = \langle \Phi_f(R)|\hat{H}_f^{(\mathrm{BO})}(R)|\Phi_f(R)\rangle,$$

with R given, which leads to the transcendental equation

$$2\gamma_f = -g_f(\rho_f)/h_f(\rho_f), \tag{6}$$

where

$$h_f(\rho) = -\frac{1}{2} + \frac{1+\mathcal{E}(\rho)}{1+S(\rho)}, \quad g_f(\rho) = \frac{1}{\rho} - \frac{1+\mathcal{C}(\rho)+2\mathcal{E}(\rho)}{1+S(\rho)},$$
$$\mathcal{C}(\rho) = \frac{1}{\rho}[1-(1+\rho)e^{-2\rho}], \quad \mathcal{E}(\rho) = (1+\rho)e^{-\rho}.$$

B. Neutral hydrogen molecule

Analogous calculations for the neutral hydrogen molecule give

$$\Phi_i(\mathbf{r}_1,\mathbf{r}_2;R) = \frac{\gamma_i^3}{\pi\left[2\left(1+S_i^2\right)\right]^{1/2}}\left[e^{-\gamma_i(r_{a1}+r_{b2})} + e^{-\gamma_i(r_{b1}+r_{a2})}\right]. \tag{7}$$

Here the electronic overlap integral $S_i = S(\gamma_i R)$ is determined by Eq. (5) and the parameter γ_i is found from the functional minimum condition

$$J_i(\gamma_i,R) = \langle \Phi_i(R)|\hat{H}_i^{(\mathrm{BO})}(R)|\Phi_i(R)\rangle$$

at a given R. This implies that γ_i is the root of the transcendental equation

$$2\gamma_i = -g_i(\rho_i)/h_i(\rho_i), \quad \rho_i = \gamma_i R, \tag{8}$$

where

$$h_i(\rho) = \frac{1 - S^2(\rho) + 2S(\rho)\mathcal{E}(\rho)}{1+S^2(\rho)},$$
$$g_i(\rho) = \frac{1}{\rho} - \frac{2[1+\mathcal{C}(\rho)] + 4S(\rho)\mathcal{E}(\rho) - \mathcal{C}'(\rho)\mathcal{E}'(\rho)}{1+S^2(\rho)},$$
$$\mathcal{C}'(\rho) = \frac{1}{\rho}\left[1 - \left(1 + \frac{11}{8}\rho + \frac{3}{4}\rho^2 + \frac{1}{6}\rho^3\right)e^{-2\rho}\right],$$

$$\mathcal{E}'(\rho) = \left(\frac{5}{8} - \frac{23}{20}\rho - \frac{3}{5}\rho^2 - \frac{1}{15}\rho^3\right)e^{-2\rho} + \frac{6\phi(\rho)}{5\rho},$$

$$\phi(\rho) = S^2(\rho)(\ln\rho + \gamma) - S^2(-\rho)E_1(4\rho) + S(\rho)S(-\rho)E_1(2\rho),$$

$\gamma \approx 0.577$ is the Euler constant, and

$$E_1(z) = \int_z^\infty \frac{e^{-t}}{t}\,dt$$

is the integral exponent. The quantities $\mathcal{C}'(\rho)$ and $\mathcal{E}'(\rho)$ are due to the exchange Coulomb interaction between electrons.

Equations (6) and (8) are solved numerically at a given R. Let us denote the result by $\tilde{\gamma}_\mu(R)$. The total electron energy of the molecule or its ion is given by the following expression without taking into account vibrations and rotations:

$$E_\mu(R) = J_\mu(\tilde{\gamma}_\mu(R),R) + \frac{1}{R}. \tag{9}$$

More accurate values of $E_\mu(R)$ can be obtained by means of the GAUSSIAN code [22]. In compliance with the general theory, they would be slightly lower than the variational values (9). According to the estimates, the difference is not more than 5%.

III. VIBRATIONAL MOTION

For the complete description of the molecule stationary states in the Born-Oppenheimer approximation, the electron functions (4) and (7) should be multiplied by the wave functions of the nuclei vibrational motion,

$$\Psi_{\mu,v_\mu}(R,\mathbf{r}_e) = \chi_{\mu,v_\mu}(R)\Phi_\mu(R,\{\mathbf{r}\}), \quad \mu = i,f,$$

where $\{\mathbf{r}\}$ is the set of the electron coordinates and χ_{μ,v_μ} describes the vibrational stationary state with the quantum number $v_\mu = 0,1,\ldots$. The potential energy of molecule vibrations is conveniently modeled by the Morse potential

$$V(R) = D_e[e^{-2a(R-R_e)} - 2e^{-a(R-R_e)}], \tag{10}$$

where R_e is the equilibrium internuclear separation. The energy levels in the potential (10) have the form

$$E_v = -\frac{a^2}{2M}\left(\beta - v - \frac{1}{2}\right)^2, \quad v = 0,1,\ldots, \tag{11}$$

where $\beta = \sqrt{2MD_e}/a$ and $M = M_aM_b/(M_a + M_b)$ is the reduced mass of the nuclei.

The quantity (11) can be considered as the spectrum of the anharmonic oscillator

$$E_v = \omega_e\left(v + \tfrac{1}{2}\right) - \omega_e x_e\left(v + \tfrac{1}{2}\right)^2 - D_e,$$

the parameters ω_e and x_e of which are directly connected with the Morse potential parameters D_e, a, and R_e. In our case these parameters can be obtained by minimization of the total energy functionals (9) with respect to R. However, major theoretical models of quantum chemistry give overestimated frequency values of ω_e up to 10%. Thus, to correct the results achieved by means of the GAUSSIAN code, corresponding scaling factors [23,24] were obtained. The method [21] used in this paper is also not an exception. Therefore, in the present paper we use the more accurate values of the parameters ω_e, x_e, and D_e cited in Ref. [25]. Wave functions normalized to the unity that correspond to the vibrational levels (11) are given by the expression

$$\chi_v(R) = N_v z^{\beta-v-1/2} e^{-z/2} L_v^{2\beta-2v-1}(z), \tag{12}$$

where

$$N_v = \left[\frac{av!(2\beta - 2v - 1)}{\Gamma(2\beta - v)}\right]^{1/2},$$

$$z = 2\beta e^{-(R-R_e)}, \quad v = 0,1,\ldots,$$

and L is the Laguerre polynomial.

A. Dyson orbital

In the traditional ADK and MO-ADK models, the core of an atom or an ion is regarded as frozen; its state does not change after the removal of the tunneling electron. However, the electron wave functions of the core electrons in a neutral molecule and in a molecular ion are generally different. This difference is the electronic analog of the Franck-Condon factor, which is stronger for the few-electron systems, in particular, for the hydrogen molecule under consideration in this paper. To account for the differences between the core electronic functions, the Dyson orbital should be used, which corresponds to the overlap integral between the electronic configurations of a neutral molecule in the initial state and of its ion in the final state,

$$\Psi_{fi}^{(\text{Dyson})}(\mathbf{r}) = \int_0^\infty dR\,\chi_{f,v_f}^*(R)\chi_{i,v_i}(R) \times \int \Phi_f^*(R,\mathbf{r}')\Phi_i(R;\mathbf{r},\mathbf{r}')d^3r'. \tag{13}$$

The importance of the Dyson orbital usage in studying the ionization of molecules was emphasized in Ref. [26].

Taking into account the small magnitude of the classical vibration amplitude compared to the equilibrium internuclear separation, expression (13) can be simplified

$$\Psi_{fi}^{(\text{Dyson})}(\mathbf{r}) \approx \langle f,v_f|i,v_i\rangle\tilde{\Phi}(R_{ef},R_{ei};\mathbf{r}).$$

Here

$$\langle f,v_f|i,v_i\rangle = \int_0^\infty \chi_{f,v_f}^*(R)\chi_{i,v_i}(R)dR \tag{14}$$

is the vibrational overlap integral. Its absolute square is the Franck-Condon factor. In Ref. [27] analytical recurrent formulas for the integral (14) were derived within the harmonic oscillator model. In the case of $v_i = 0$ the results practically do not differ from those obtained in the Morse potential model. However, with the growth of v_i the role of the anharmonic effects increases dramatically. For example, for the H_2 molecule at $v_i = 1$ the vibrational overlap integrals differ by ~10%, at $v_i = 2$ by ~25%, and at $v_i = 3$ by more than twice as much. Therefore, in taking into account the excitations of the vibrational degrees of freedom the harmonic oscillator model appears to be just qualitative. Thus the integral (14) for the Morse potential can be found only numerically with specified values of parameters.

In a strong laser field the collisionless orientation of the molecular axes occurs along the direction of the light wave electric vector [28–32]. The direct observation of the molecule orientation influence on its ionization probability in a strong laser field was carried out in Ref. [33]. Here we will not take into account this effect, assuming that the ionizing laser pulse is sufficiently short. Accounting for the orientation for the long pulses is not difficult. Therefore, in Eq. (13), R is used instead of $\mathbf{R}$. The final result will be averaged with respect to the random orientation of the molecule relative to the radiation polarization vector.

Further, in Eq. (13), the electronic overlap integral

$$\tilde{\Phi}(R_{ef},R_{ei};\mathbf{r}) = \int \Phi_f^*(R_{ef},\mathbf{r}')\Phi_i(R_{ei};\mathbf{r},\mathbf{r}')d^3r',$$

where R_{ei} and R_{ef} are the equilibrium internuclear separations in the neutral molecule and in its ion, respectively, is transformed by taking into account the axial and reflection symmetries of the integrand functions in Eqs. (4) and (7),

$$\begin{aligned}\tilde{\Phi}&(R_{ef},R_{ei};\mathbf{r})\\ &= \frac{2\left(\tilde{\gamma}_i^2\tilde{\gamma}_f\right)^{3/2}}{\left[\pi\left(1+\tilde{S}_i^2\right)(1+\tilde{S}_f)\right]^{1/2}}\\ &\quad\times e^{-\tilde{\gamma}_i\mathcal{R}_c(R_{ei};r,\cos\theta)}\int_0^\infty\int_{-1}^{+1} e^{-\tilde{\gamma}_i\mathcal{R}_c(R_{ei};r',\zeta')}\\ &\quad\times[e^{-\tilde{\gamma}_f\mathcal{R}_c(R_{ef};r',\zeta')}+e^{-\tilde{\gamma}_f\mathcal{R}_c(R_{ef};r',-\zeta')}]d\zeta' r'^2 dr'.\end{aligned}$$

Here

$$\tilde{\gamma}_\mu \equiv \tilde{\gamma}_\mu(R_{e\mu}),\quad \tilde{S}_\mu \equiv S(\tilde{\gamma}_\mu R_{e\mu}),\quad \mu = i,f,$$
$$\mathcal{R}_c(R_e;r,\zeta) = \left[r^2+\tfrac{1}{4}R_e^2 - rR_e\zeta\right]^{1/2}.$$

The angle θ specifies the direction of the vector $\mathbf{r}$ with respect to the molecule axis. Integration is performed numerically.

The obtained Dyson orbital must be expanded in series over spherical functions

$$\Psi_{fi}^{(\mathrm{Dyson})}(\mathbf{r}) = \langle f,v_f|i,v_i\rangle \sum_{l=0,2,\ldots}\mathcal{R}_l(r)Y_{l0}(\hat{\mathbf{r}}),$$

where summands with the odd orbital and nonzero quantum numbers are absent due to the symmetry of the hydrogen-molecule ground state (the ${}^1\Sigma_g{}^+$ term). It is convenient to construct the quantity

$$\mathcal{T}_l(\kappa_{\mathrm{var}},r) = \mathcal{R}_l(r)(\kappa_{\mathrm{var}}r)^{1-1/\kappa_{\mathrm{var}}}e^{\kappa_{\mathrm{var}}r} \tag{15}$$

out of the obtained Dyson orbitals.

A parameter κ_{var} is fitted so that at large values of r, the value of $\mathcal{T}_l(\kappa_{\mathrm{var}},r)$ tends to a constant limit that is independent of r. The values of v_i, v_f, and l are supposed to be given. Practically, the required value of κ can be found by fitting so that at the r variation in the interval [25 35] a.u., the value of Eq. (15) would be constant, for example, within five decimal places. In this case the values of C and C_l used in Eq. (1) are obtained automatically within an accuracy of up to four decimal places.

The coefficient κ in the asymptotic form of the radial wave function (2) is calculated out of the ionization potential. For many diatomic molecules, the ionization potentials between the ground vibrational states I_{exp} are presented in Ref. [34]. In the Born-Oppenheimer approximation, the values of κ in the case of the ionization from the excited vibrational states are obtained by the formula

$$\kappa_{fi} = \sqrt{2\left(I_{\mathrm{exp}} - E_{v_i}^{(i)} + E_0^{(i)} + E_{v_f}^{(f)} - E_0^{(f)}\right)}, \tag{16}$$

where $E_{v_i}^{(i)}$ and $E_{v_f}^{(f)}$ are given by Eq. (15) with the corresponding parameters for both a neutral molecule and its ion, respectively.

As demonstrated in calculations for the H_2, HD, and D_2 molecules, the values of κ_{var} and κ_{fi} differ from each other within 10%. Therefore, in Eqs. (1) and (2) we will use the experimental values κ_{fi} for the parameter κ and we will use the variational values κ_{var} for the calculation of the parameters C and C_l. Only these κ values produce the constant limit of Eq. (15) at $r \to \infty$ and therefore the C and C_l constants.

Thus the Dyson orbital (13) for the hydrogen molecule with $r \to \infty$ gets the asymptotic form

$$\begin{aligned}\Psi_{fi}^{(\mathrm{Dyson})}(\mathbf{r}) \approx \langle f,v_f|i,v_i\rangle C\kappa_{fi}^{3/2}(\kappa_{fi}r)^{1/\kappa_{fi}-1}e^{-\kappa_{fi}r}\\ \times\sum_{l=0,2,\ldots}C_lY_{l0}(\hat{\mathbf{r}}).\end{aligned} \tag{17}$$

The structure of this expression corresponds completely to the asymptotic form of the wave function in the MO-ADK model (1) and (2). From the form of the function (17), we can conclude that the molecule tunneling ionization rate is proportional to the Franck-Condon factor.

The equilibrium internuclear separations practically do not depend on the isotope molecule composition for the hydrogen molecule and its ion. We present the values of the asymptotic constants for the hydrogen molecule,

$$\kappa_{\mathrm{var}} = 1.1616,\quad C = 3.4017,\quad C_0 = 0.9954,$$
$$C_2 = 0.0958,\quad C_4 = 0.0015.$$

The values of C_l obtained by the variational method differ from those obtained in Refs. [19,35] by the model potential methods. It should be noted that the authors of Ref. [19] pointed out a possible dependence of C_l on the choice of the model. The coefficients C_2 and C_4 demonstrate the electronic configuration deviation from the spherical form. In our model this deviation appears to be more significant compared to the model potentials [19,35].

The values of the Franck-Condon factors are presented in Table I. It is obvious that with an increase of the vibrational quantum number of the neutral molecule the Franck-Condon factors initially grow. This is explained by the fact that

TABLE I. Values of the Franck-Condon factors in the hydrogen molecule of various isotope compositions in various vibrational states in the absence of the external fields at $v_f = 0$ and at the equilibrium internuclear separation R_e.

	$\lvert\langle f,0\lvert i,v_i\rangle\rvert^2$		
v_i	H_2	HD	D_2
0	9.308×10^{-2}	6.239×10^{-2}	3.221×10^{-2}
1	2.662×10^{-1}	2.101×10^{-1}	1.359×10^{-1}
2	3.298×10^{-1}	3.106×10^{-1}	2.554×10^{-1}
3	2.178×10^{-1}	2.549×10^{-1}	2.772×10^{-1}
4	7.822×10^{-2}	1.228×10^{-1}	1.890×10^{-1}
5	1.398×10^{-2}	3.400×10^{-2}	8.292×10^{-2}

the effective internuclear separation of the neutral molecule grows with an increase of the vibrational quantum number, approaching the equilibrium internuclear separation in the molecular ion. A further decrease of the Franck-Condon factors is due to an increase of the oscillation number of the vibrational wave function in the states with larger values of v_i.

It should be noted that the importance of accounting for the Franck-Condon factors for the description of the experimental results on the tunneling ionization of D_2 molecules was pointed out in Ref. [18]. In Ref. [19], accounting for the motion of the nuclei in the tunneling ionization of molecules was carried out by means of averaging the tunnel effect probability over the internuclear separation R. The probability distribution of R values in turn was determined from the absolute square of the neutral-molecule vibrational wave function. The molecular ion vibrational state was not taken into account in Ref. [19]. Evidently, this approach should be considered as quasiclassical.

Plotted in Fig. 1 is the difference of the results calculated by Eq. (22) (the results of the calculation are presented below) from the standard MO-ADK model [19] with no account taken of the laser radiation influence on the vibrational motion, which is considered in Sec. III B. Our model uses an experimental value of the ionization potential I_{exp}. The MO-ADK model from Ref. [19] requires the use of the Hartree-Fock ionization potential $I(R)$ as a function of the internuclear separation R. It is known that the Hartree-Fock value is lower than the experimental one, so at lower intensities our results appear to be significantly less than those obtained within the model from Ref. [19].

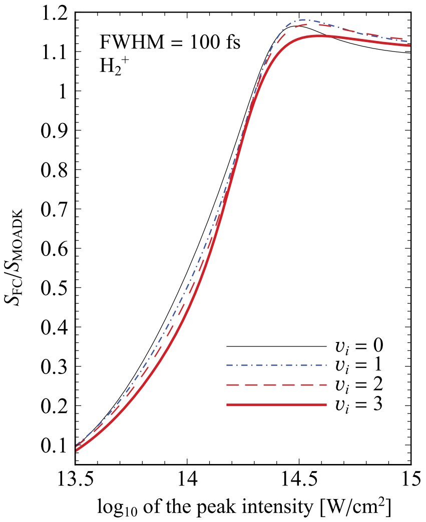

FIG. 1. (Color online) Ratio of the results calculated by Eq. (22) to the standard MO-ADK model [19] with the improved electron wave-function parameters [35]. Here S_{FC} is the number of ions calculated by Eq. (22) for ionization of a H_2 molecule from the vibrational state with a given quantum number v_i to all possible states of the $H_2{}^+$ ion and S_{MOADK} is the number of ions calculated within the MO-ADK model [19]. The full width at half maximum (FWHM) is equal to 100 fs. The change of the nuclei vibrational motion in the laser field (Sec. III B) is not taken into account.

B. Laser field influence on molecular vibrational motion

An external laser field modifies the parameters of the molecule vibrations. Such an effect was taken into account in Ref. [36] in the Born-Oppenheimer approximation in the field of monochromatic linearly polarized laser radiation. The response of the molecular vibrations to the external field is determined by the tensor of the dynamic molecular polarizability $\alpha_{ij}(\omega,\mathbf{R})$ depending on the internuclear separation, where ω is the frequency of the external field. For a nonrotating molecule at the specified internuclear separation R, the change of energy in the external monochromatic field (the quadratic dynamic Stark effect) is given by the expression

$$\Delta E(\omega,\mathbf{R}) = -\tfrac{1}{4}\,\alpha(\omega,\mathbf{R})F^2.$$

Hereinafter F is the laser field intensity amplitude

$$\alpha(\omega,\mathbf{R}) = \alpha_{\parallel}(\omega,R)\cos^2\theta + \alpha_{\perp}(\omega,R)\sin^2\theta,$$

$\alpha_{\parallel}$ and $\alpha_{\perp}$ are the longitudinal and transversal components of the tensor of the dynamic polarizability respective to the molecule axis, respectively, and θ is the angle between the molecule axis and the vector of radiation polarization.

In Ref. [36] it was demonstrated that the consideration of the polarization effect of the laser field on the molecule leads to the change of the molecule vibrational parameters. In the adiabatic approximation, when the nuclei vibration cycle is significantly shorter than the time of changing the laser radiation intensity, the vibrational parameters are modified according to the formulas

$$R_e = R_e^{(0)}\left[1 + \frac{\alpha^{(1)}F^2}{4M\omega_e^2 R_e^{(0)}}\right], \tag{18}$$

$$\omega_e = \left[\omega_e^{(0)2} - \frac{\alpha^{(2)}F^2}{4M}\right]^{1/2}. \tag{19}$$

Here

$$\alpha^{(\nu)} = \left.\frac{\partial^\nu \alpha}{\partial R^\nu}\right|_{R=R_e^{(0)}}, \quad \nu = 1,2.$$

The superscript (0) corresponds to the frequency ω_e and the separation R_e in the absence of external fields.

The tensor components $\alpha_{ij}(\omega,R)$ can be obtained, for example, by the GAUSSIAN code. The Franck-Condon factors exposed to the field begin to differ from those presented in Table I for a field-free molecule. The largest Franck-Condon factors from Table I give the least response to the external field. The small Franck-Condon factors change more appreciably. The results of the calculation of the radiation influence on the vibrational motion and the change hereupon of the dependence of the tunnel effect probability on the radiation intensity are shown in Fig. 2 (the details of the calculation are presented below). It should be noted that consideration of the laser radiation influence on the vibrational motion leads to a change of the curve slopes compared to the ADK-like models. The difference between the curve slopes is greater when the magnitude of the vibrational energy quantum is smaller. Thus, for the H_2 molecule ($\omega_e = 2.005 \times 10^{-2}$ a.u.) the ionic yields at an intensity of 10^{15} W/cm^2 will differ by 1.4 times; for the D_2 molecule ($\omega_e = 1.421 \times 10^{-2}$ a.u.)

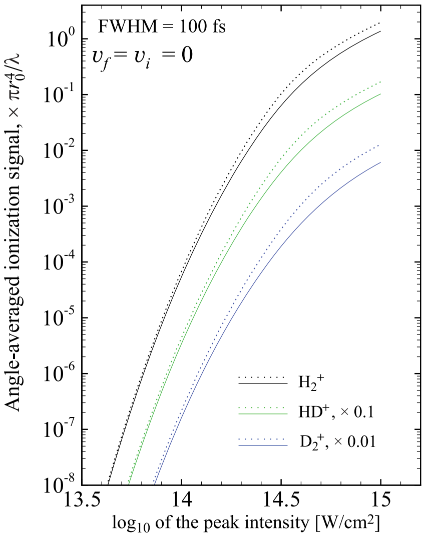

FIG. 2. (Color online) Ionization signal averaged over the orientations of the H_2 (top lines), HD (middle lines), and D_2 (bottom lines) molecules as a function of the peak intensity in the focus. The ionization occurs from the ground vibrational state. The solid lines correspond to the results obtained by taking into account the laser field influence on the molecular vibrational parameters (18) and (19) and the dotted lines correspond to the results obtained without this influence. For clarity, the ionization probabilities for the HD^+ and ${D_2}^+$ ions are reduced 10 and 100 times, respectively.

the results will be twice as much. This difference becomes smaller with an increase in v_i. It practically vanishes in the H_2 molecule at $v_i = 2$ and in HD and D_2 molecules at $v_i = 3$ since the Franck-Condon factors cease to depend on the intensity. This dependence can be revealed again upon the further increase of v_i when the Franck-Condon factors begin to decrease.

In Ref. [37] consideration was given to the direct influence of the laser radiation on the atomic nuclei and the subsequent modification of the potential well in which the nuclei vibrations take place. However, this mechanism is less effective compared to the one connected with the influence of the field on the molecular electrons [36].

IV. TUNNELING RATE

In a monochromatic linearly polarized laser field the average rate of the electron tunneling from a molecule is expressed by [19]

$$W_{v_f v_i}(F,\hat{\mathbf{R}}) = |\langle f,v_f|i,v_i\rangle|^2 \sum_{m'} |B_{m'}(\hat{\mathbf{R}})|^2 w_{\kappa m'}(F). \tag{20}$$

Here, according to Eq. (17),

$$w_{\kappa m'}(F) = \frac{C^2\kappa^2}{2^{|m|}|m|!}\left(\frac{2\kappa^3}{F}\right)^{2/\kappa-|m|-3/2} \exp\left(-\frac{2\kappa^3}{3F}\right),$$

$\hat{\mathbf{R}}$ is the unit vector in the molecular axis direction,

$$B_{m'}(\hat{\mathbf{R}}) = \sum_l C_l D^l_{m'm}(\hat{\mathbf{R}}) Q_{lm'},$$

the z axis is directed along the radiation polarization vector, m and m' are the projection of the tunneling electron orbital momentum on the molecular axis and on the radiation polarization direction, respectively, and

$$Q_{lm} = (-1)^{|m|}\sqrt{\frac{(2l+1)(l+|m|)!}{2(l-|m|)!}},$$

The standard designation is introduced for the Wigner D function. For the hydrogenic ${}^1\Sigma_g{}^+$ term the D-function form is significantly simplified [38],

$$D^l_{m'm}(\hat{\mathbf{R}}) = \delta_{m0}\sqrt{\frac{4\pi}{2l+1}}\, Y^*_{lm'}(\hat{\mathbf{R}}), \quad l = 0,2,\ldots.$$

The principal dependence of Eq. (20) on the vibrational state of the original molecule is connected with the dependence on the vibrational quantum number v_i in the parameter κ_{fi} determined by Eq. (16). Whereas in the MO-ADK model the tunneling rate is proportional to the squared constant factor in the asymptotic form of the wave function (2), in our model this constant factor is multiplied by the Franck-Condon factor. The important peculiarity of the proposed model is the dependence of the Franck-Condon factor on the radiation intensity via the parameters (18) and (19).

V. IONIZATION SIGNAL

Equation (20) is valid for monochromatic radiation with a spatially homogeneous intensity distribution. A close-to-real distribution of the axially symmetric light beam intensity amplitude can be modeled with the Gaussian envelope over both time and the beam diameter taking account the diffraction,

$$F(r,z,t) = \frac{F_0 r_0}{W(z)} e^{-2(\ln 2)r^2/W^2(z)} e^{-2(\ln 2)t^2/\tau^2}, \tag{21}$$

where $W(z) = r_0\sqrt{1+z^2/z_0^2}$, r_0 is the beam waist radius in the focus, $z_0 = \pi r_0^2/\lambda$ is the Rayleigh range, λ is the laser central wavelength, τ is the FWHM, r is the distance from the observation point to the beam axis, and z is the distance from the focus to the observation point along the beam axis.

The probability of the molecular ionization being located at a specified point of the focal volume by the laser pulse (21) is calculated according to the formula

$$P(F(r,z),\hat{\mathbf{R}}) = 1 - \exp\left[-\int_{-\infty}^{+\infty} W_{v_f v_i}(F(r,z,t),\hat{\mathbf{R}})dt\right].$$

For a comparison with the experiment on measuring the yield of the ions in the total focal volume it is necessary to calculate the ionization signal

$$S_0(F,\hat{\mathbf{R}}) = 2\pi n_0 \int P(F(r,z),\hat{\mathbf{R}}) r\, dr\, dz,$$

where n_0 is the concentration of the neutral molecules in the laser pulse front. An integration technique over the focal volume was proposed in Ref. [39]. Two-dimensional integration over r and z can be reduced to one-dimensional numerical integration over strength (or intensity) and to analytical integration on the isoenergetic surfaces inside the focal volume. This gives rise to the only one-dimensional factor $r_0^4 n_0/\lambda$:

$$S_0(F,\hat{\mathbf{R}}) = \frac{\pi^2 r_0^4 n_0}{3\lambda}\int_0^{I_0} P(F,\hat{\mathbf{R}})c(I)[3+c^2(I)]dI,$$

where

$$c(I) = \sqrt{\frac{I_0}{I}-1}$$

and I_0 is the peak radiation intensity in the focus. Recall that in atomic units, the intensity of the linearly polarized monochromatic radiation is connected with the intensity amplitude by the simple relation $I = F^2$.

If the orientation of molecules with respect to the polarization vector is random, then the ionization signal averaged over the orientation of molecules has the form

$$S_1(F) = \frac{1}{4\pi}\int S_0(F,\hat{\mathbf{R}})d\Omega_R.$$

For the hydrogen ${}^1\Sigma_g{}^+$ term, this expression is simplified,

$$S_1(F) = \int_0^{\pi/2} S_0(F,\theta_R)\sin\theta_R d\theta_R. \tag{22}$$

Nevertheless, its value is obtained by numerical integration only.

VI. NUMERICAL RESULTS AND DISCUSSION

The calculations of the quantity (22) have been carried out for H_2, HD, and D_2 molecules at a FWHM equal to 100 fs. It should be noted that the vibrational cycle in the molecule is ∼10 fs; therefore, the adiabatic approximation mentioned in Sec. III B is satisfied. The possibility of the initial neutral molecule existing in the excited vibrational state ($v_i = 0,1,2,3$) has been taken into account. The created ion has been considered in the ground state only ($v_f = 0$). The ionization signal (22) averaged over the molecule orientations has been calculated as a function of the radiation peak intensity in focus.

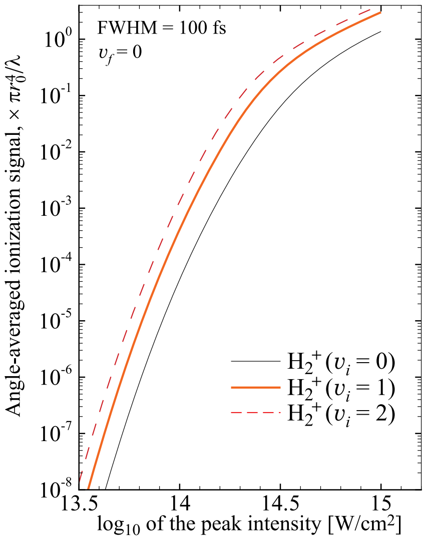

FIG. 3. (Color online) Ionization signal averaged over the orientations of the H_2 molecule (22) as a function of the radiation peak intensity in the focus.

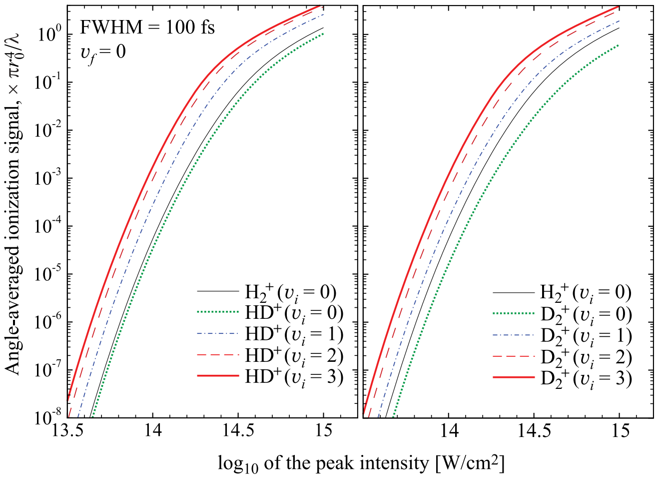

FIG. 4. (Color online) Same as Fig. 3 but for HD and D_2 molecules. The results on H_2 ionization from the ground vibrational state are presented for comparison.

The results of the calculations are presented in Figs. 3 and 4. They correspond to the ionization of an AB molecule from the ground electronic state and a vibrational state with the quantum number v_i to the ground vibrational state of an AB^+ ion. It is evident that with a v_i increase from 0 to 3 the ionization increases (anti-Stokes enhancing). At the higher excitations of the neutral-molecule vibrations, the effect is suppressed. The yield of the ions stops growing and even decreases. These graphs are not shown in the figures. This is due to the weak overlap of the vibrational wave functions as follows from the values of the corresponding Franck-Condon factors (see Table I). The results of a H_2-molecule ionization of HD and D_2 from the ground vibrational states are presented in the figures for comparison.

The vibrational frequencies of the investigated molecules are related to one another as

$$\omega_e(D_2) : \omega_e(HD) : \omega_e(H_2) \approx 1 : 1.2 : 1.4$$

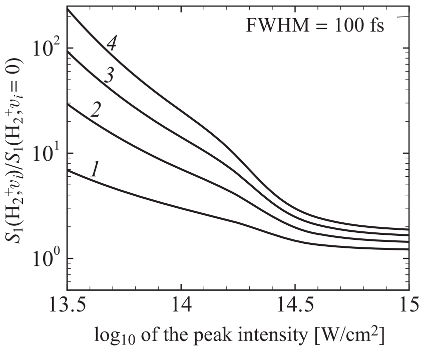

FIG. 5. Ionization signal ratio for neutral H_2 molecules in excited vibrational states to the signal for the molecules in the ground vibrational state. The values of the vibrational quantum number v_i are indicated. All possible vibrational states of the $H_2{}^+$ ions are taken into account.

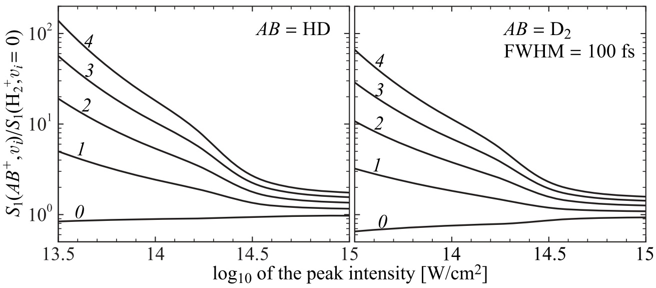

FIG. 6. Ionization signal ratio for neutral HD and D_2 molecules in various vibrational states to the signal for H_2 molecules in the ground vibrational state. The values of the vibrational quantum number v_i are indicated. All possible vibrational states of the molecular ions are taken into account.

due to the growth of the reduced mass while their Morse potential depth is approximately the same [25]. If the Franck-Condon factor is maximal for the D_2 molecule at $v_i = 3$, then for the H_2 molecule it reaches the maximum value at $v_i = 2$ and is suppressed at higher vibrational energies (see Table I).

In an experiment the vibrational states of the resulting ion, as a rule, are not fixed. Therefore, the rate (20) is to be summed up over all possible quantum numbers v_f,

$$W_{v_i}(F,\hat{\mathbf{R}}) = \sum_{v_f} W_{v_f v_i}(F,\hat{\mathbf{R}}). \qquad (23)$$

Equation (23) includes the Stokes channels and does not take into account the dissociative ionization that we neglect.

Figure 5 demonstrates the role of the motion of nuclei at the H_2-molecule ionization. The diagram demonstrates the ratio of the ionization signal for the neutral molecules in the excited vibrational states to the signal for molecules in the ground vibrational state. The ionization signal is calculated by Eq. (22) and the ionization rate is summed up over all vibrational states of the molecular ion according to Eq. (23).

Figure 6 presents the ratio of the ionization signal for deuterated hydrogen molecules in various initial vibrational states to the ionization signal for a H_2 molecule in the ground vibrational state. All vibrational states of the molecular ions are taken into account according to Eq. (23). The results presented demonstrate that the isotope optical separation can be implemented by prepumping the vibrational degrees of freedom of the deuterated hydrogen molecules.

VII. CONCLUSION

In the present paper sequential consideration is given to the nuclei vibrational motion influence on molecule tunneling ionization. The change of the equilibrium internuclear separation in the field owing to the molecular electronic polarizability dependence on the internuclear separation is taken into account. The possibility of the vibrational ion quantum number changing compared to the vibrational quantum number of a neutral molecule is also taken into account. This effect allows one to set up the ionization of molecules of a specified isotope composition provided the excitation of the vibrational quantum states of the neutral molecules of the required isotope composition by the IR radiation is carried out beforehand.

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